Understanding the Environmental Transmission Electron Microscope

Wagner, Jakob Birkedal

Publication date:
2012

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Rafal E. Dunin-Borkowski, Institute for Microstructure Research, Forschungszentrum Jülich, Germany

Jörg R. Jinschek, FEI Europe, Eindhoven, The Netherlands

DTU Cen
Center for Electron Nanoscopy

Towards Understanding the Environmental Transmission Electron Microscope

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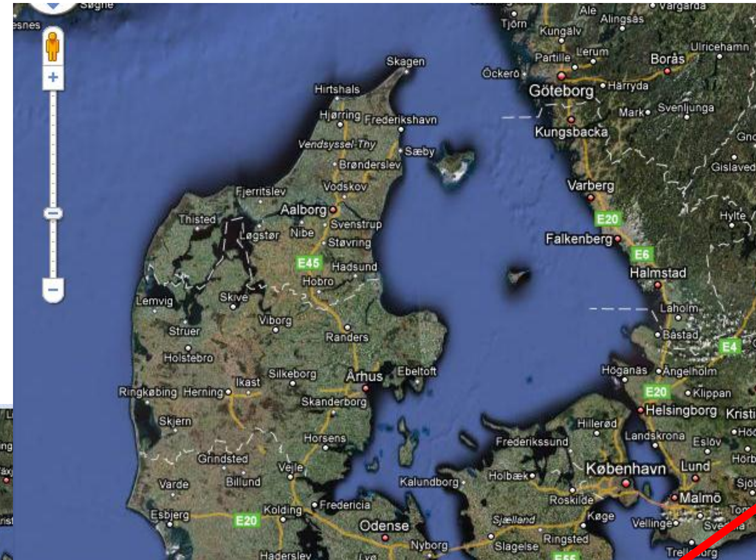
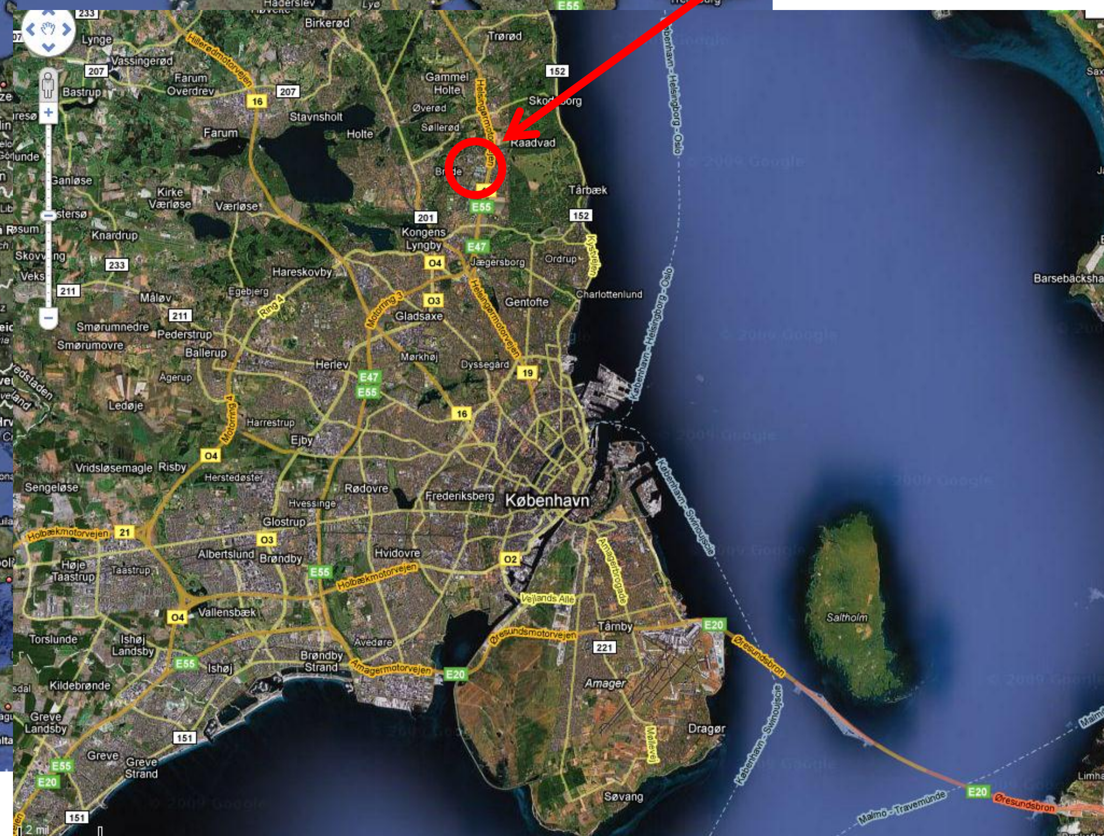
Where are We?



DTU



DTU Center for Electron Nanoscopy

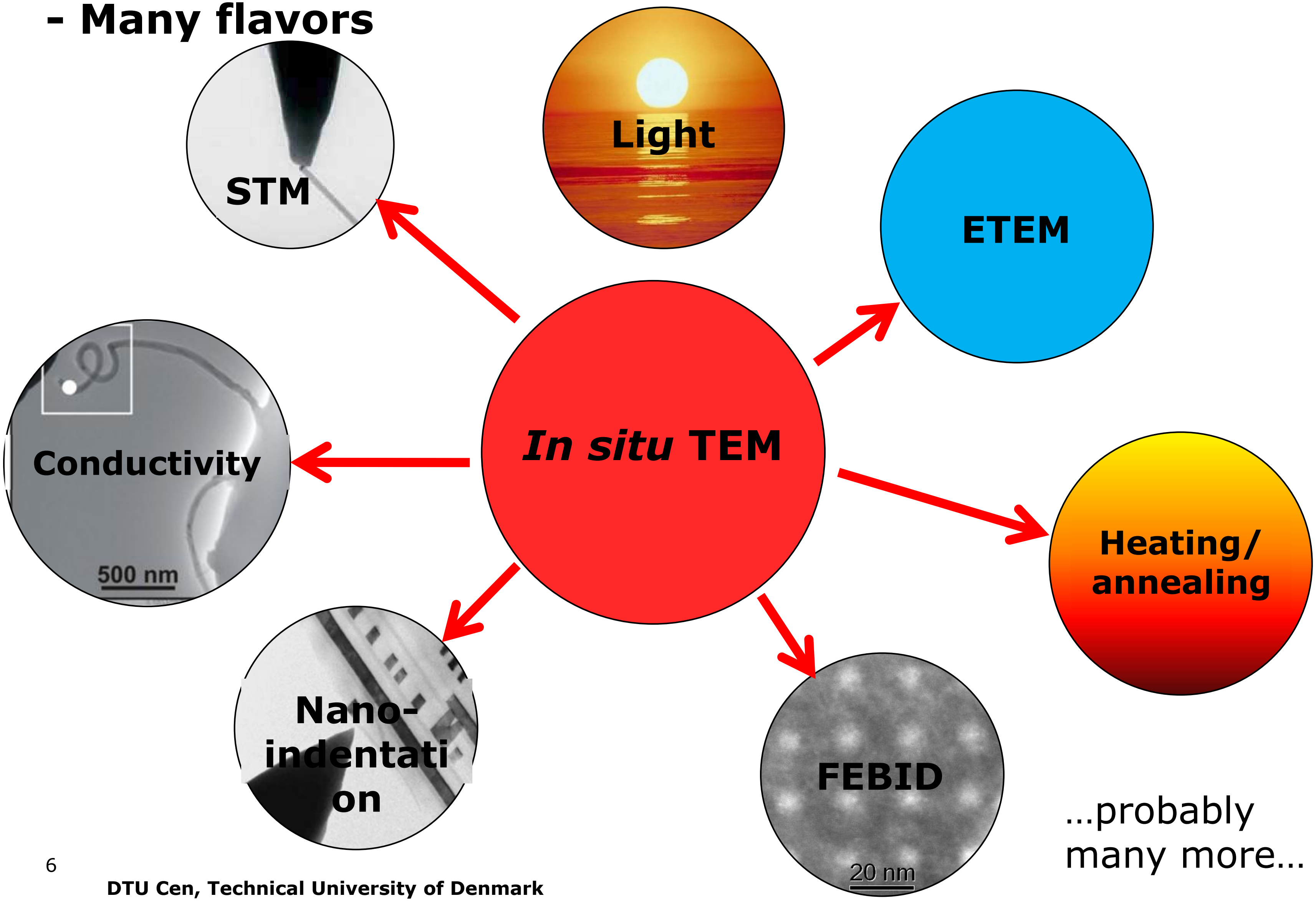
- Realized by a generous donation from the A.P. Møller og Hustru Chastine Mc-Kinney Møller's Fond til Almene Formaal
- DKK 100,000,000 ~ €14,000,000
- Grant announced in January 2006
- *"Establish a World Class Facility with a unique suite of advanced electron microscopes, in a purpose-built building"*
- Inaugurated in December 2007

- Hosting 7 electron microscopes
  - 2 high-end TEMs (1 ETEM)
  - 1 work horse TEM
  - 2 dual beam SEM/FIB
  - 2 SEM

What is *In Situ* Microscopy

- …depends on who you ask…
- "The class of experiments allowing observations of materials' dynamic response to an externally applied stimulus as it happens inside the microscope"
- The *in situ* observations may be accompanied by simultaneous measurements of the materials' properties to directly establish structure-functionality relationships

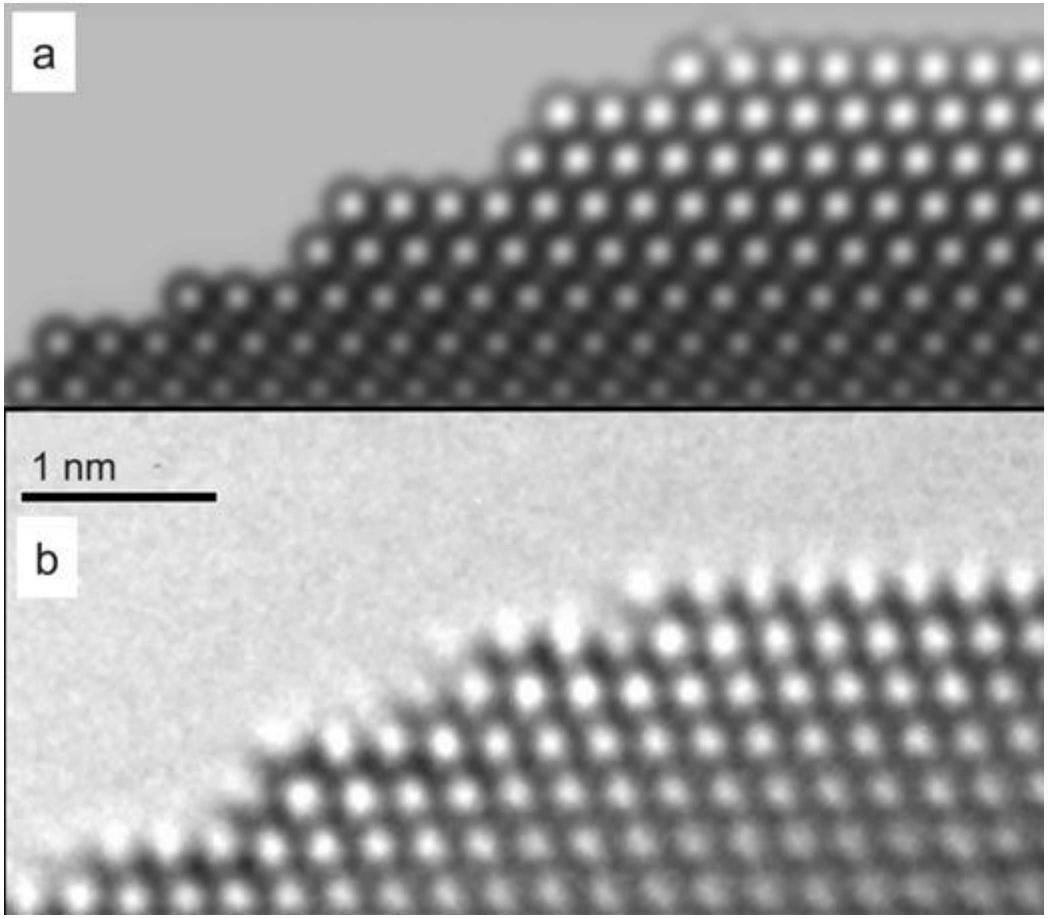
In Situ Microscopy
- Many flavors



...probably
many more...

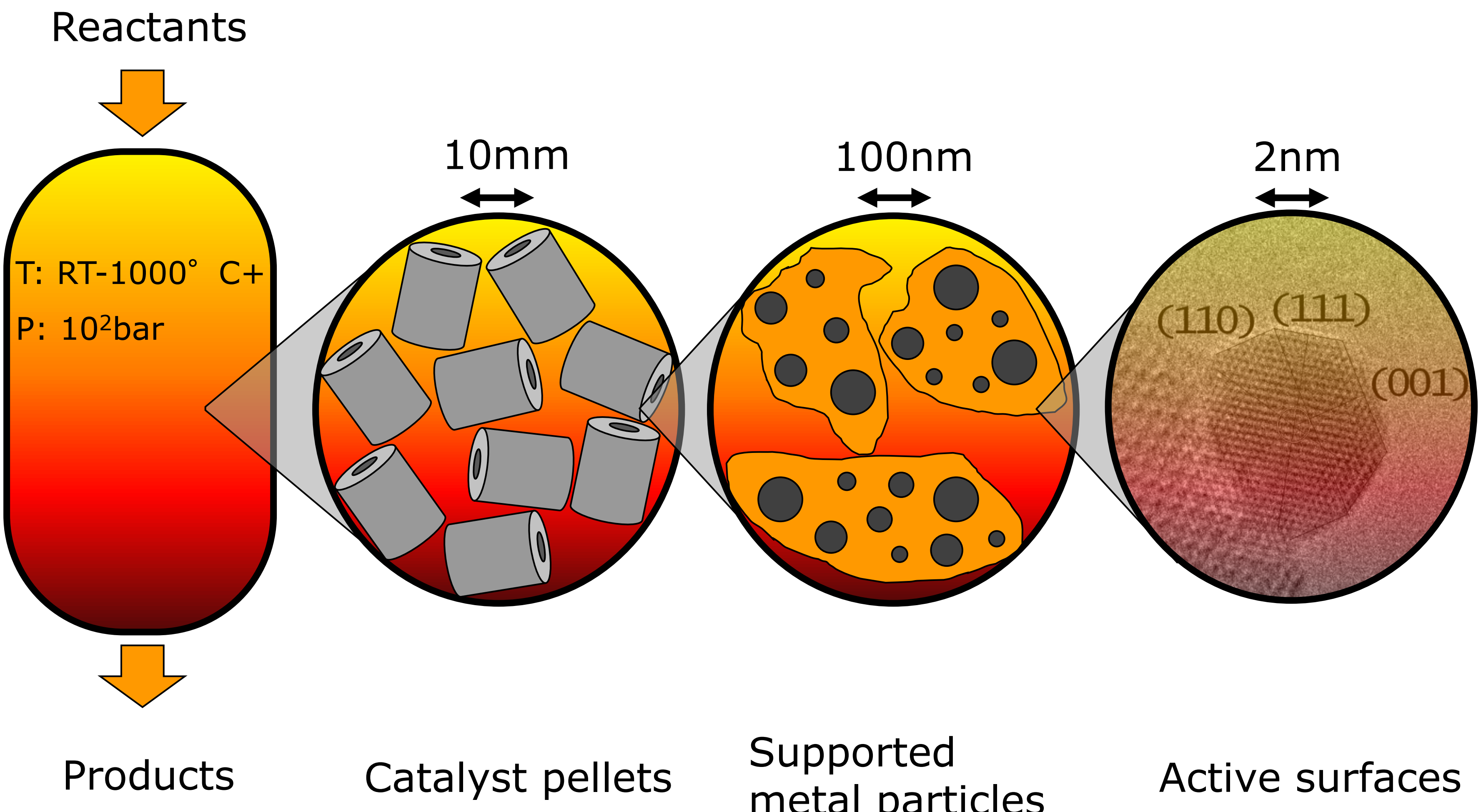
What are We Trying to Achieve?

- Obtain high-resolution information
- Dynamic responses of materials as they are exposed to reactive gases at elevated temperatures
- Surface structure of materials in various environments
- Morphology of materials in different surroundings



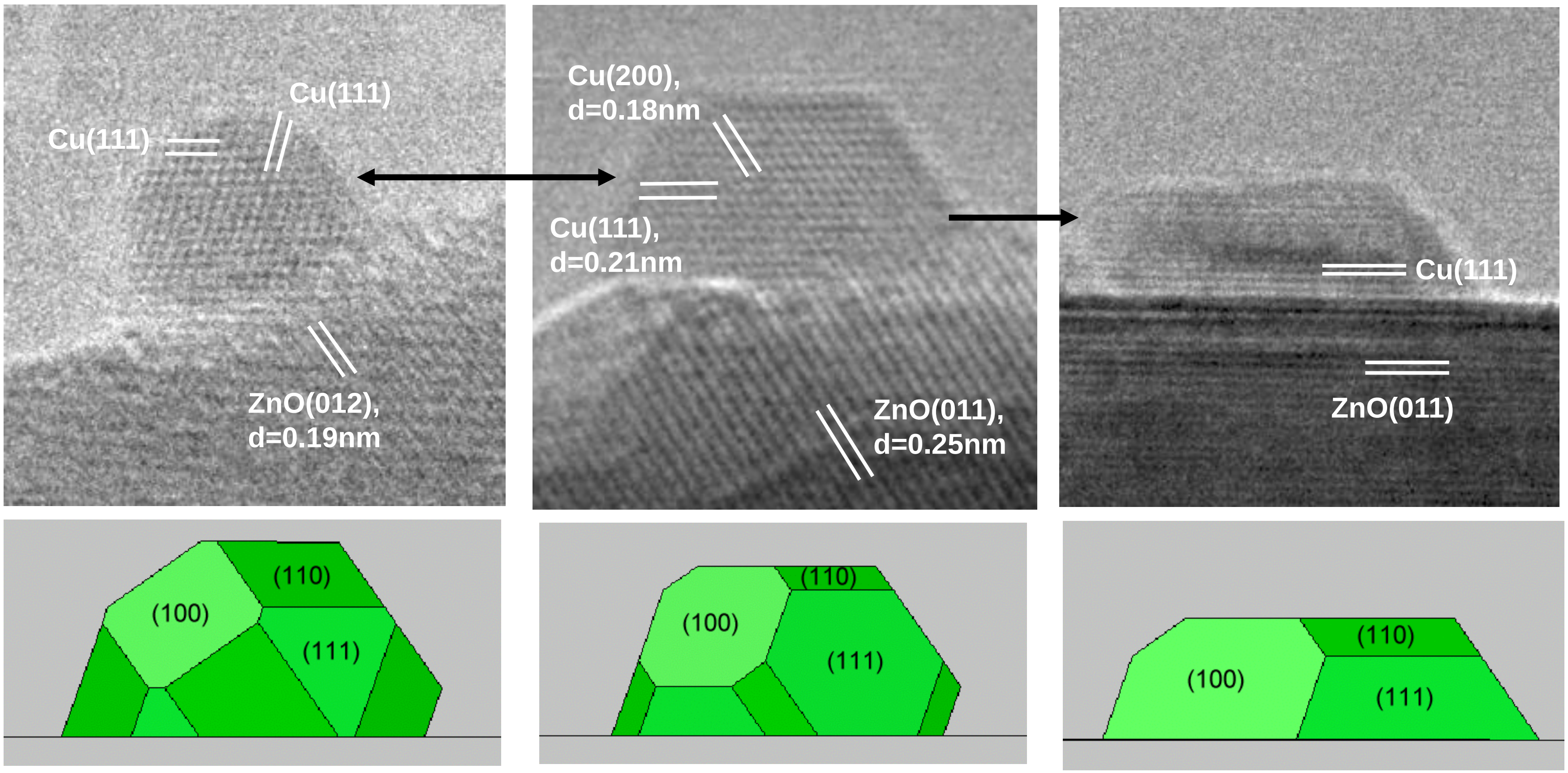
Dang Sheng Su, Timo Jacob, Thomas W. Hansen, Di Wang, Robert Schlögl, Bert Freitag, and Stephan Kujawa, *Angew. Chem.* **47**, 5005 (2008)

A Look Inside the Catalytic Reactor



Why do We Want to do *In Situ* Microscopy? Equilibrium shapes versus gas composition

H_2/H_2O | H_2 | H_2/CO

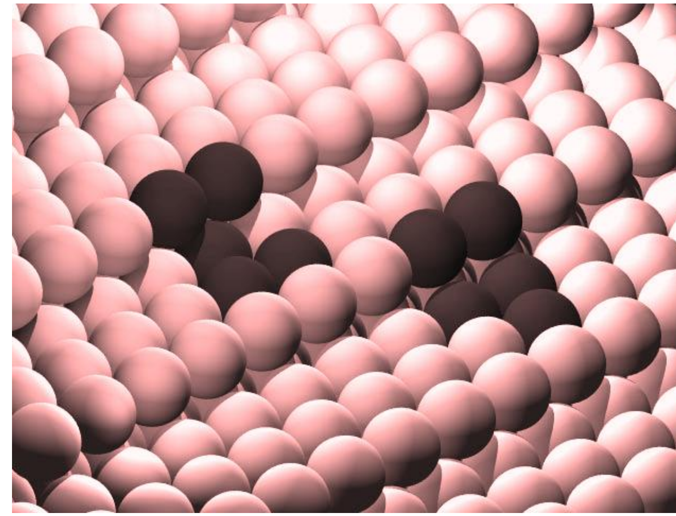


1.5mbar, H_2/H_2O=3/1, 220°C | 1.5mbar, 220°C | 1.5mbar, H_2/CO=95/5, 220°C

J. B. Wagner *et al.* *Science* **395,** 2053 (2002).

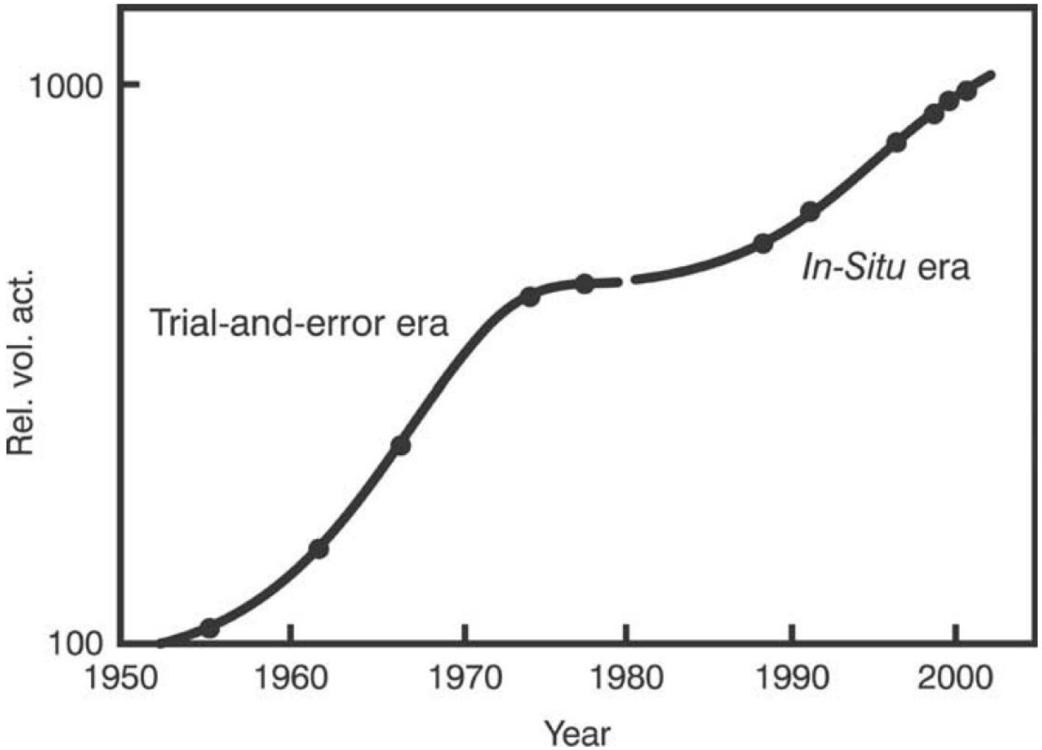
Why do We Want to do *In Situ* Microscopy? ...continued

- Conventional electron microscopy does not always tell the full story
  - Samples are (usually) not in their operational environment
- Materials respond dynamically to changes in environment
  - Surface reconstruction due to gas adsorption
  - Phase transitions
  - Growth
- Lack of temporal resolution
- Essential for establishing structure-activity correlations



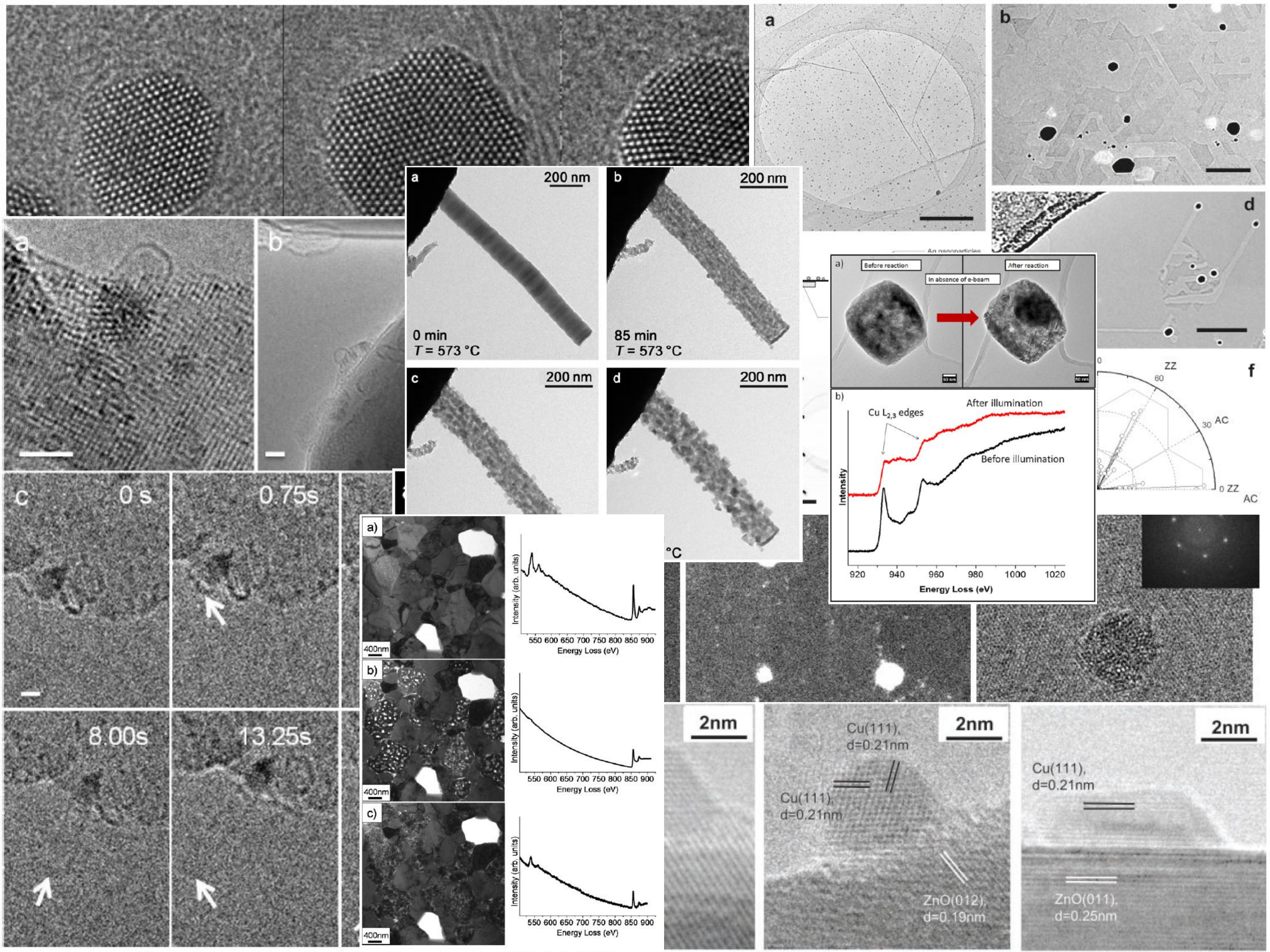
b_5 sites on the (105) surface of Ru. These sites were proposed to be the active sites for N_2 splitting (van Hardeveld and von Montfoort Surf. Sci. 4 (1966) 396. Figure from T.W. Hansen *et al. Catal Lett.* **84,** 7 (2002).

In Situ Techniques



Evolution of activity of industrial HDS catalysts,
B.M. Moyse, World Refining Jan/Feb (2001) 28
H. Topsøe, J. Catal. 216, 155 (2003)

- *In situ* XRD
  - Phase determination
  - Good for large areas
- *In situ* EXAFS, FTIR
  - Coordination
  - Chemical bonding
- Average values
  - No local information
- *In situ* TEM
  - Gives local information
- Etc…

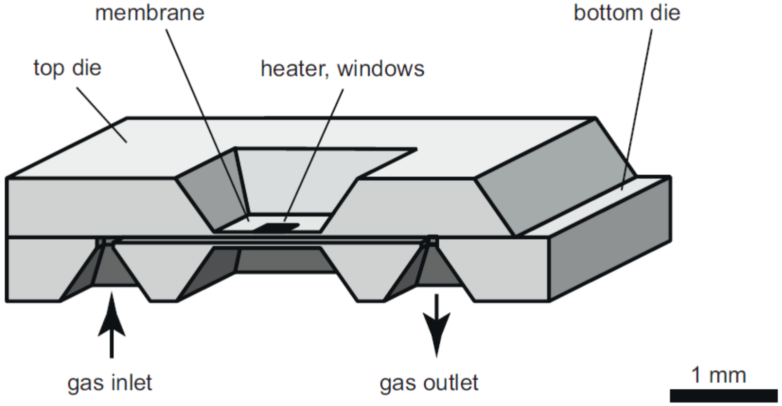


a
b
c
d
f
0 s
0.75s
8.00s
13.25s
200 nm
0 min
T = 573 °C
85 min
T = 573 °C
°C
Ag nanoparticles
a)
Before reaction
In absence of e-beam
After reaction
50 nm
b)
Cu $L_{2,3}$ edges
After illumination
Before illumination
Intensity
Energy Loss (eV)
920
940
960
980
1000
1020
ZZ
AC
60
30
0
0 ZZ
400nm
Intensity (arb. units)
550 600 650 700 750 800 850 900
2nm
Cu(111),
d=0.21nm
ZnO(012),
d=0.19nm
ZnO(011),
d=0.25nm

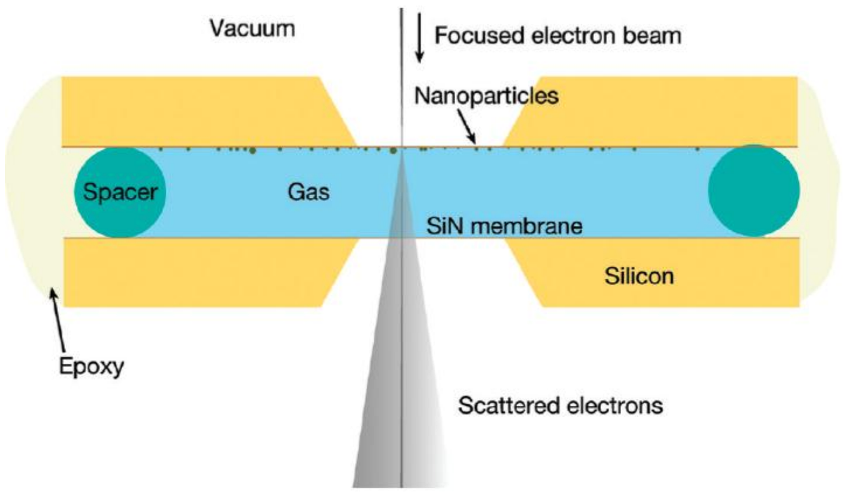
Imaging in the fog of gas

Can we get a clear view...?

Windowed Design



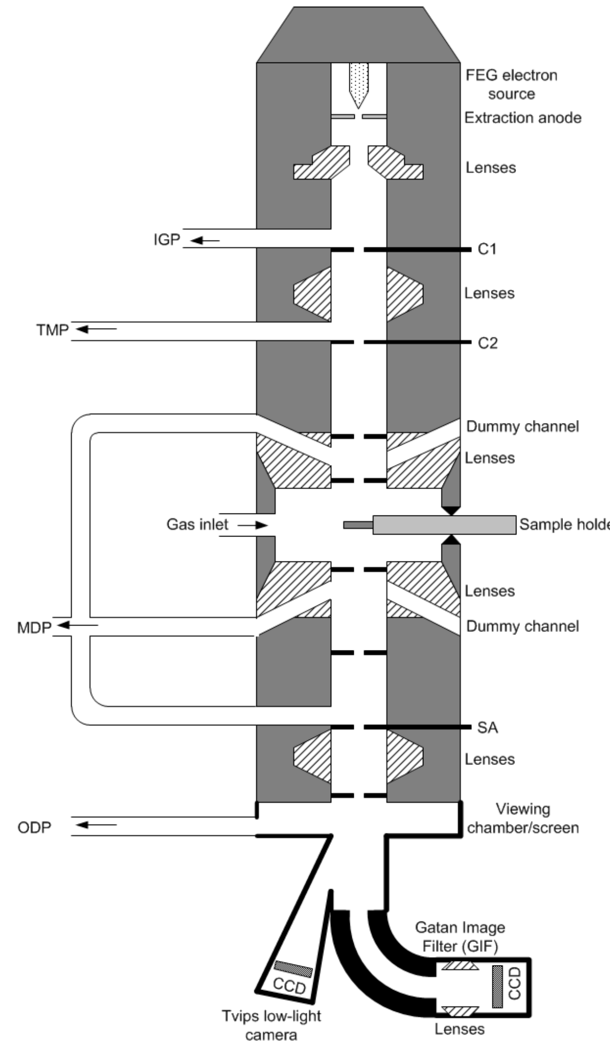
J. F. Creemer *et al.*, Ultramicroscopy 108, 993 (2008)



N. de Jong *et al.*, Nano Letters 10, 1028 (2010)

Differentially pumped Column

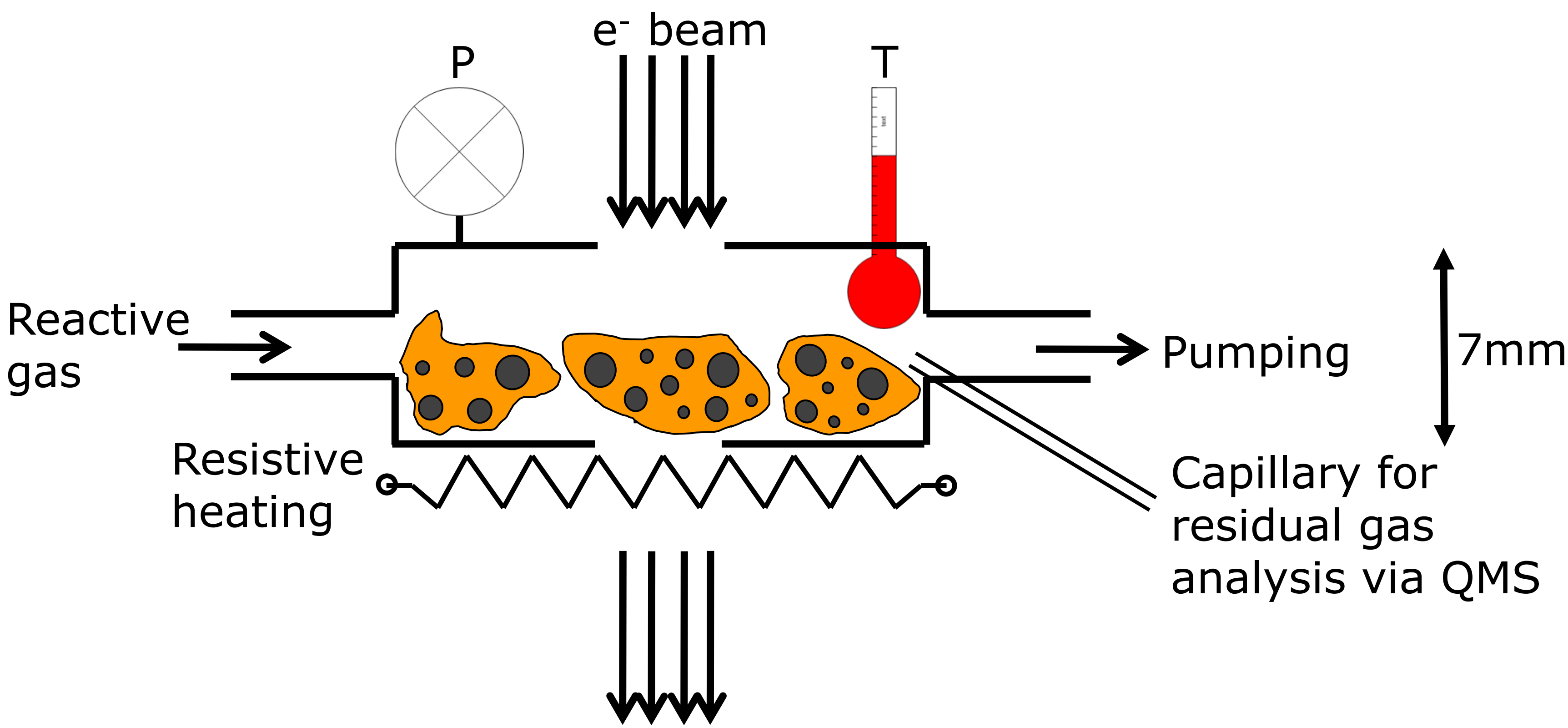
- FEI Titan 80-300
  - Highly stable platform
  - Variable high tension 80, 200, 300kV
  - Field emission electron source (XFEG)
  - Monochromator
  - Objective lens aberration corrector
  - De-contaminator (plasma cleaner)
- Differential pumping system
  - Gas is leaked in
  - Two sets of diffusion limiting apertures
  - Turbo molecular pump (TMP)
  - Ion getter pump (IGP)



T. W. Hansen, J. B. Wagner and R. E. Dunin-Borkowski, *Mater. Sci. Tecnol.*, 26, 1338 (2010)

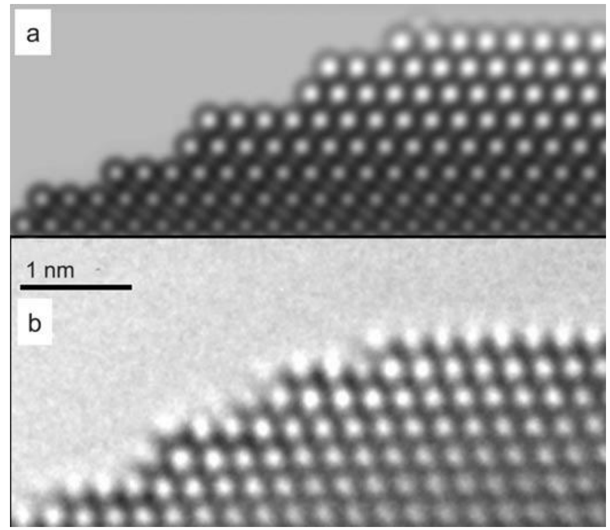
The Environmental Cell
- not really a cell...

- Main purpose: to confine the gas to the vicinity of the sample thus making the gas path length along the direction of the electrons as short as possible

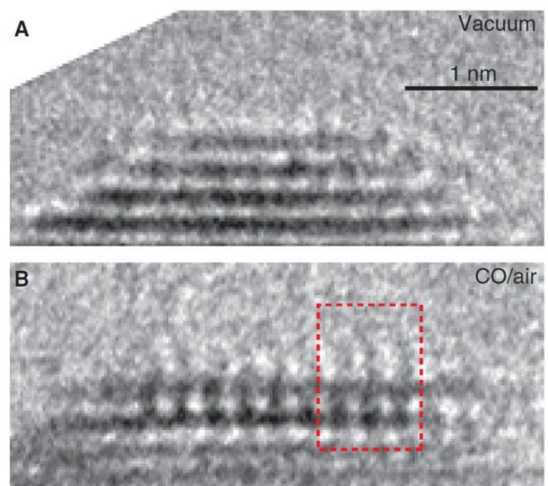


Quantitative ETEM !?

- Obtain high-resolution information
- Dynamic responses of materials as they are exposed to reactive gases at elevated temperatures
- Surface structure of materials in various environments
- Morphology of materials in different surroundings
- Adsorbed molecules



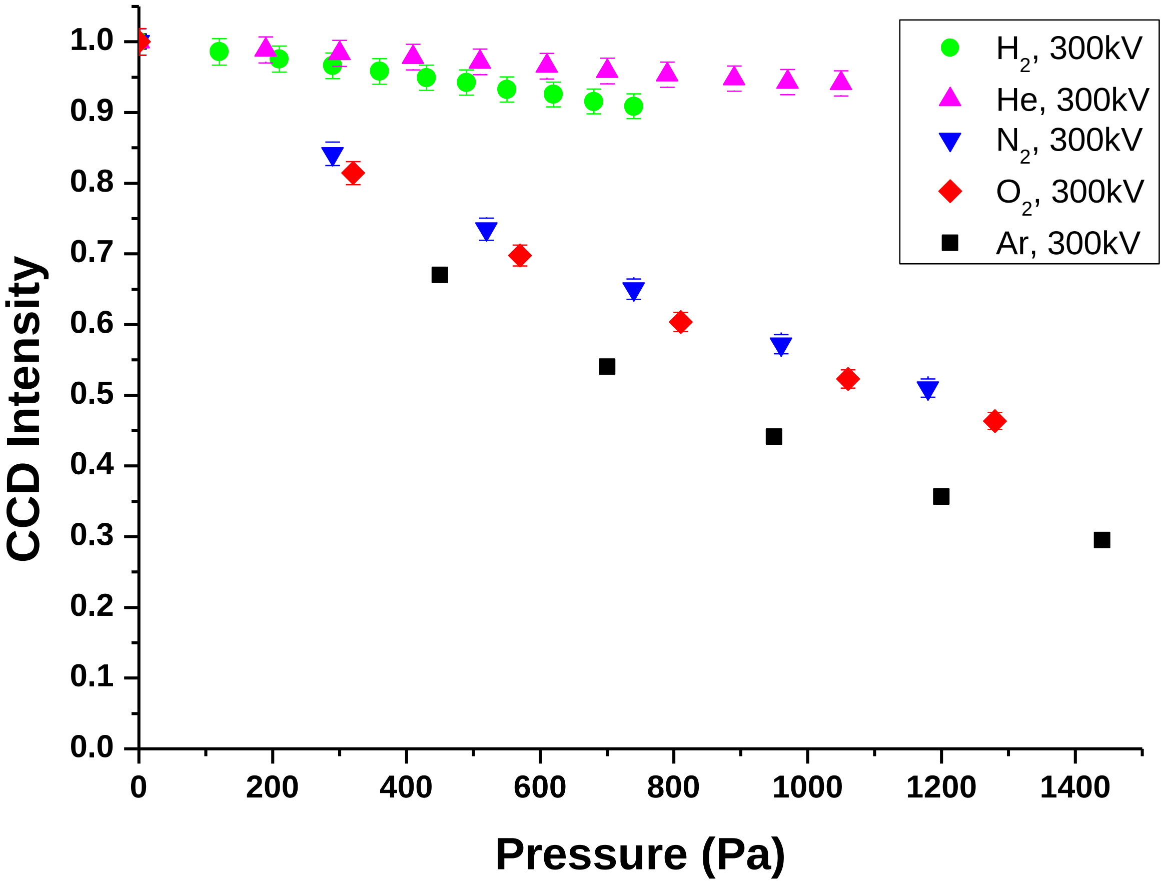
D. S. Su *et al.*, *Angew. Chem.* 47, 5005 (2008)



H. Yoshida *et al.*, *Science* 335, 317 (2012)

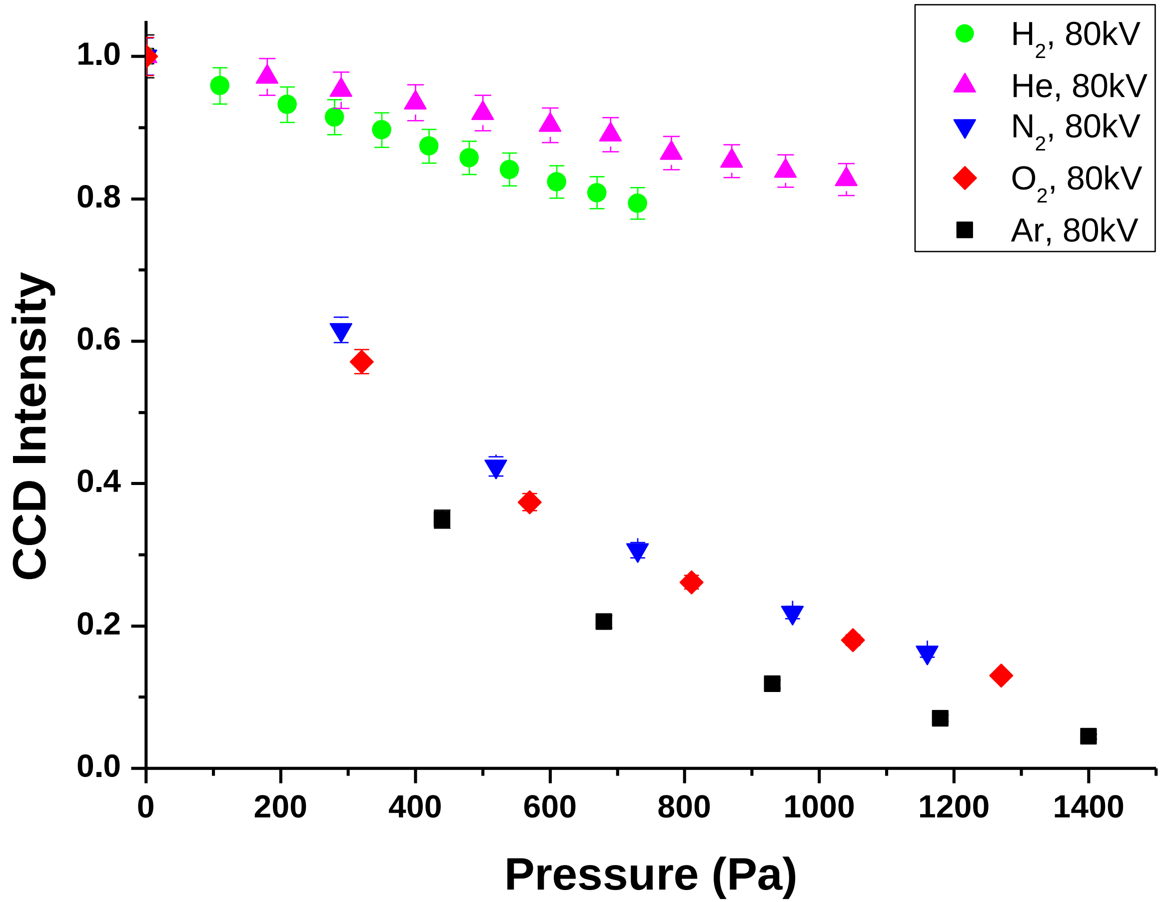
Loss of Intensity

- Main effect of imaging in gas is loss of intensity
- Intensity measured on a bottom mounted camera as a function of argon pressure in the sample region
- At high Ar pressure, >1400Pa, the intensity passing through the objective lens has decreased by more than a factor of 2 at 300kV
- Increasing pressure leads to loss of temporal resolution



Loss of Intensity

- Main effect of imaging in gas is loss of intensity
- Intensity measured on a bottom mounted camera as a function of argon pressure in the sample region
- At high Ar pressure, >1400Pa, the intensity passing through the objective lens has decreased by more than a factor of 2 at 300kV
- As high a primary energy is desired due to a longer mean free path in the gas phase
- Increasing pressure leads to loss of temporal resolution



Apparent Mean Cross Sections and Mean Free Paths

- Intensities fitted to:

$$\frac{I}{I_0} = e^{-x/\lambda}$$

- Mean free path:

$$\lambda = \frac{1}{\sigma n}$$

- Assuming ideal gas:

$$pV = NRT \Rightarrow n = \frac{N}{V} = \frac{P}{RT} \Rightarrow \lambda = \frac{RT}{\sigma P}$$

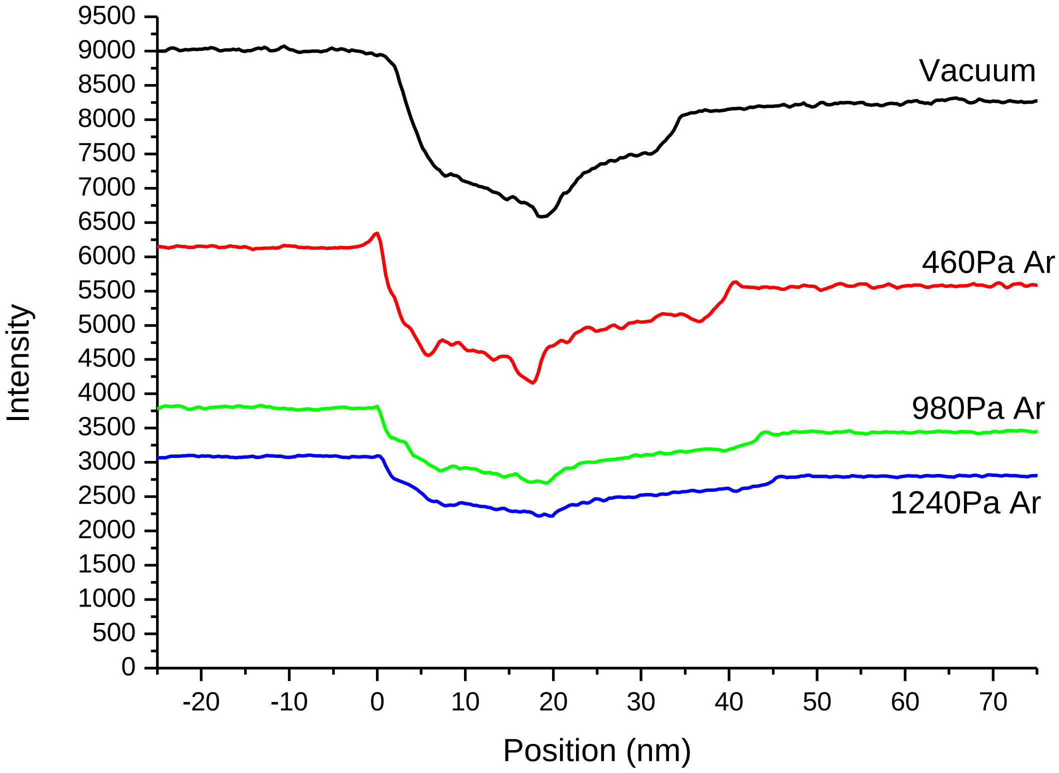
- Fit function becomes:

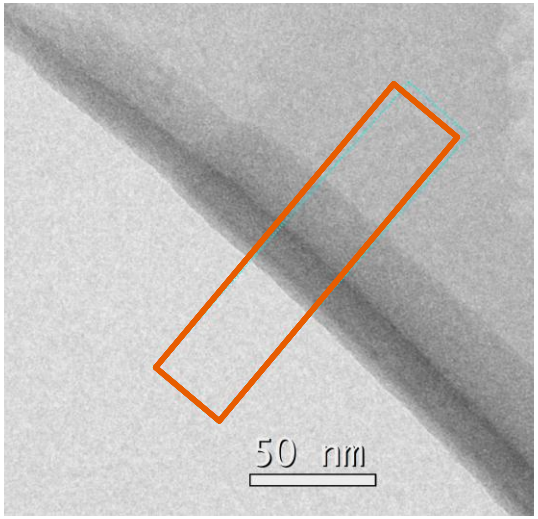
$$\frac{I}{I_0} = e^{-\frac{\sigma P}{RT}\times 7.5\times 10^{-3}\,m}$$

	σ[m²]	λ(500Pa)[10^{-3}m]
80kV, H_2	1.8E-22	46
80kV, He	9.7E-23	85
80kV, N_2	8.9E-22	9
80kV, O_2	9.1E-22	9
80kV, Ar	1.3E-21	7
200kV, N_2	4.1E-22	20
200kV, O_2	4.1E-22	20
200kV, Ar	6.0E-22	14
300kV, N_2	3.2E-22	26
300kV, O_2	3.0E-22	28
300kV, Ar	4.5E-22	19

Contrast and Loss of intensity (Bright field imaging)

- How does the contrast of BF images change with gas pressure?
- 2.7mrad objective aperture (semiangle)
- Illumination conditions kept constant





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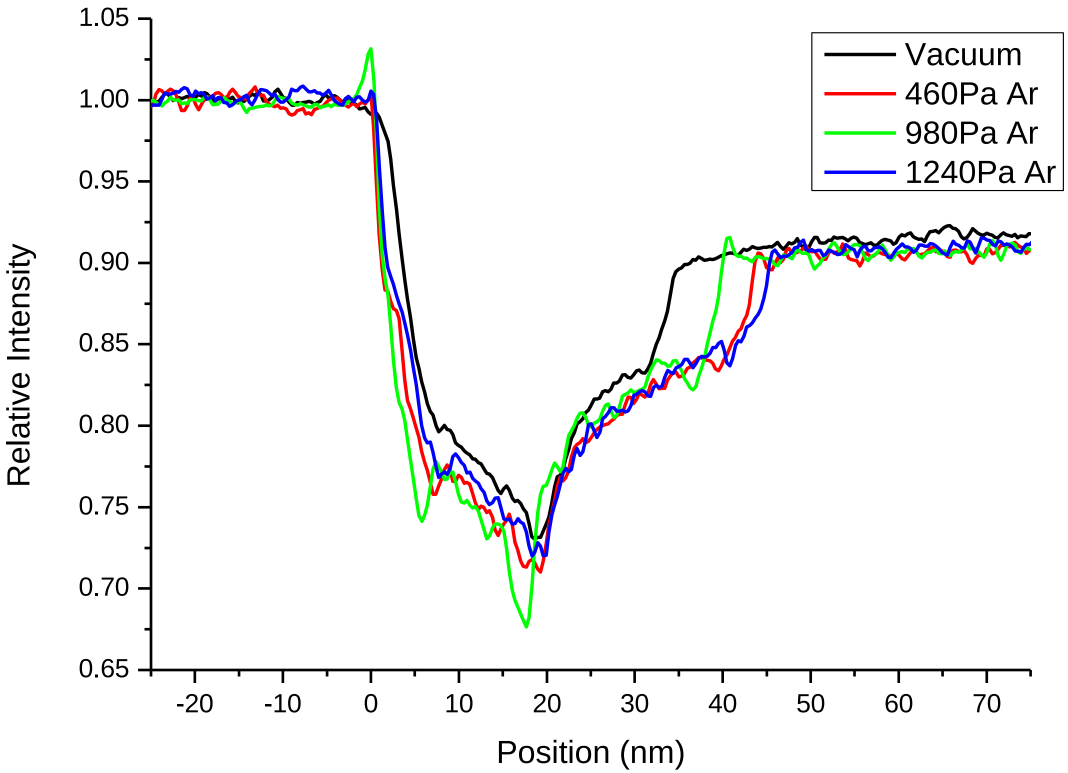
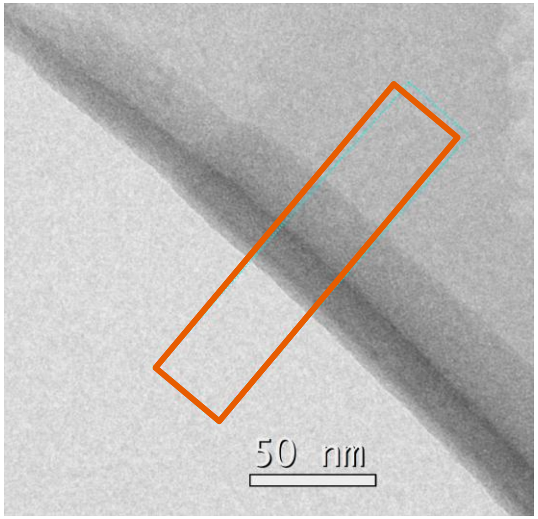
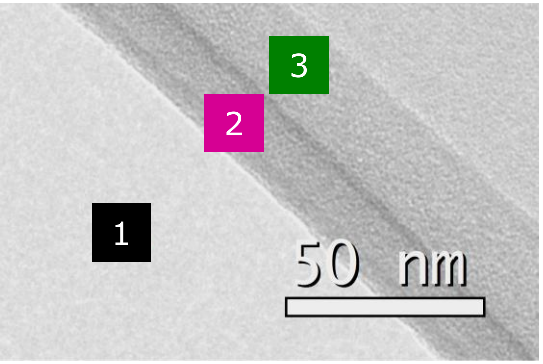
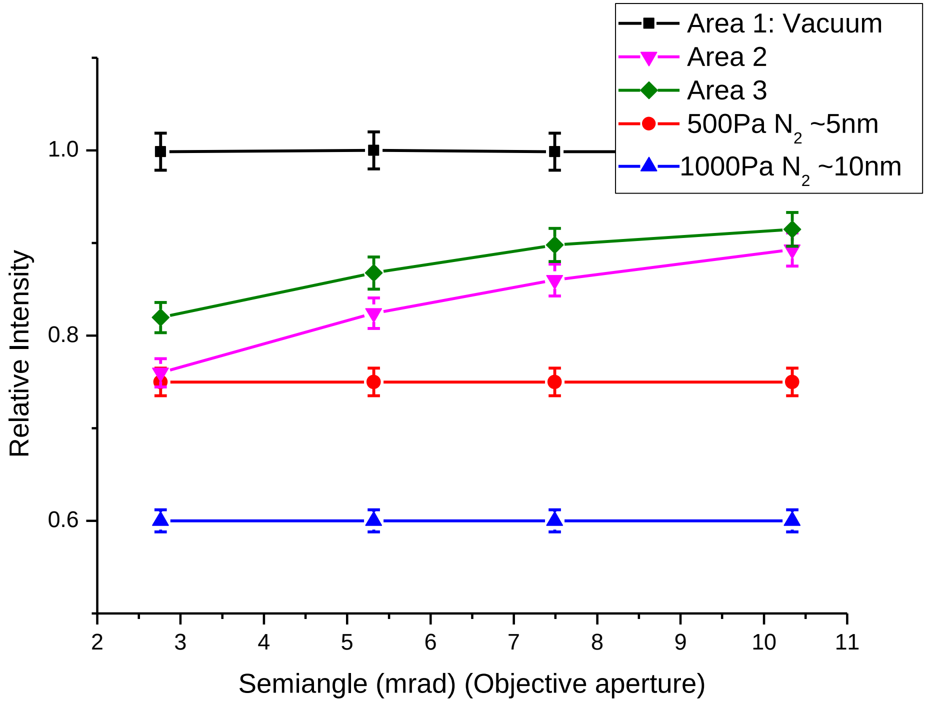




Contrast and Loss of intensity (Bright field imaging)

- Carbon Film
- Compared to N_2 gas
- 1000 Pa N_2 between pole pieces corresponds to approx. 10nm thick solid

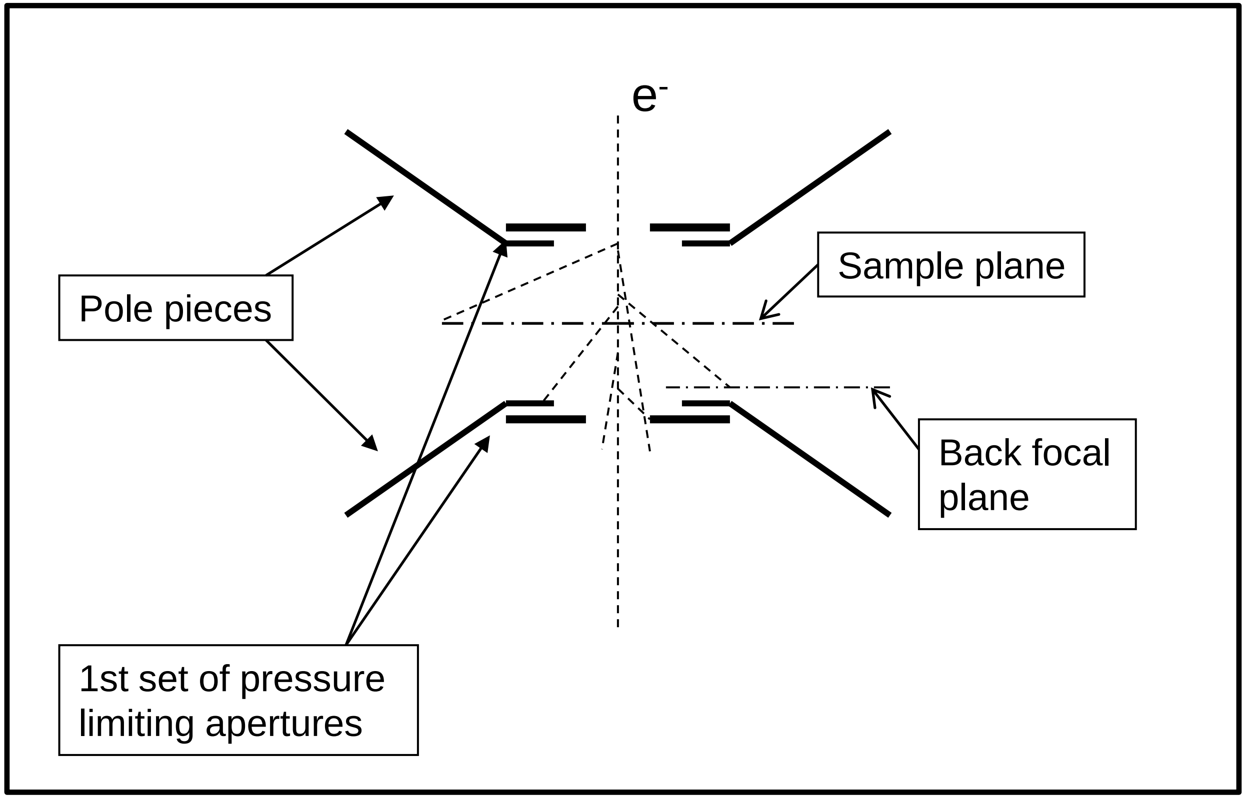




- Very little depence on the objective aperture for the gas related intensity loss
- The ‘contrast’ from the gas scattering appears higher than for corresponding area density of solid

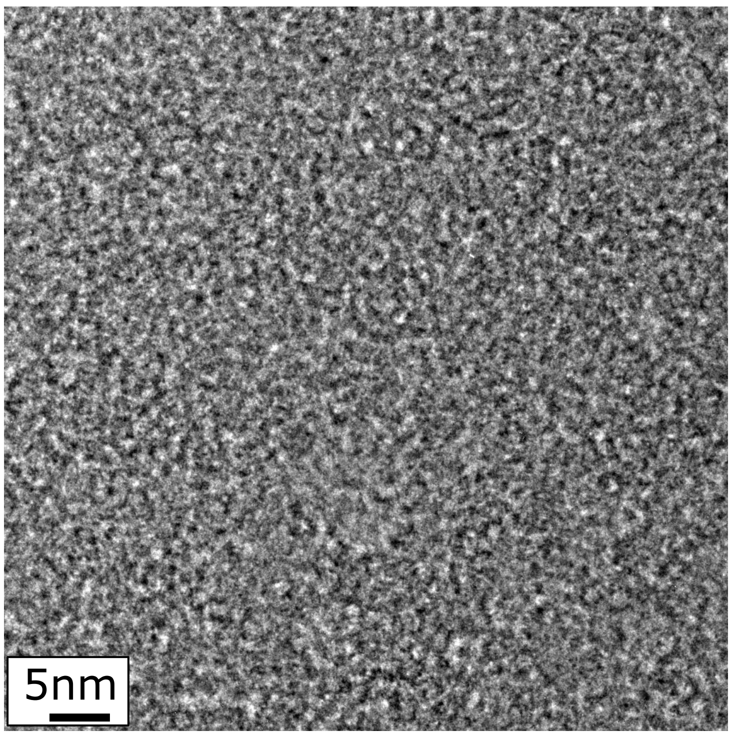
Geometry of scattering

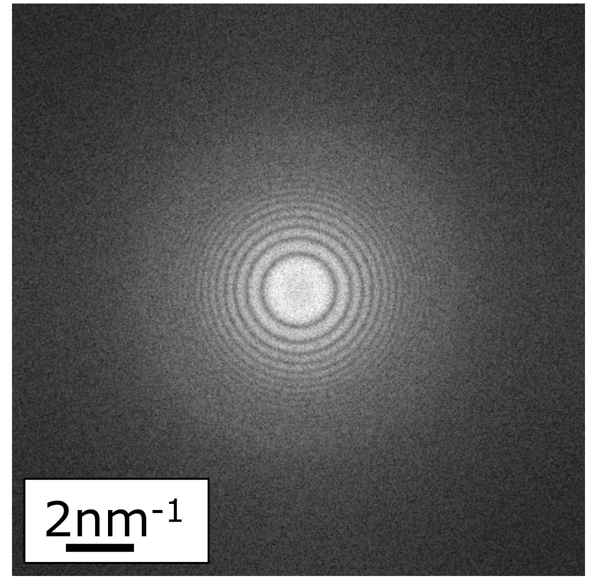
- Scattering takes place over several millimeters.
- Back focal plane and image plane not well-defined for gas scattering

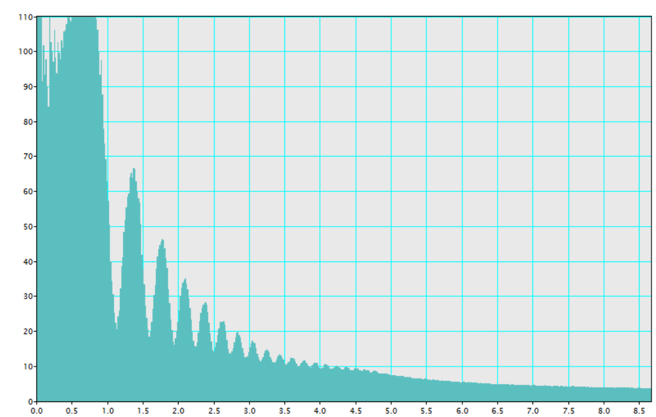


Resolution and contrast in the presence of gas (Phase contrast)

- Effects of imaging in gas can be observed from the power spectrum of amorphous carbon film

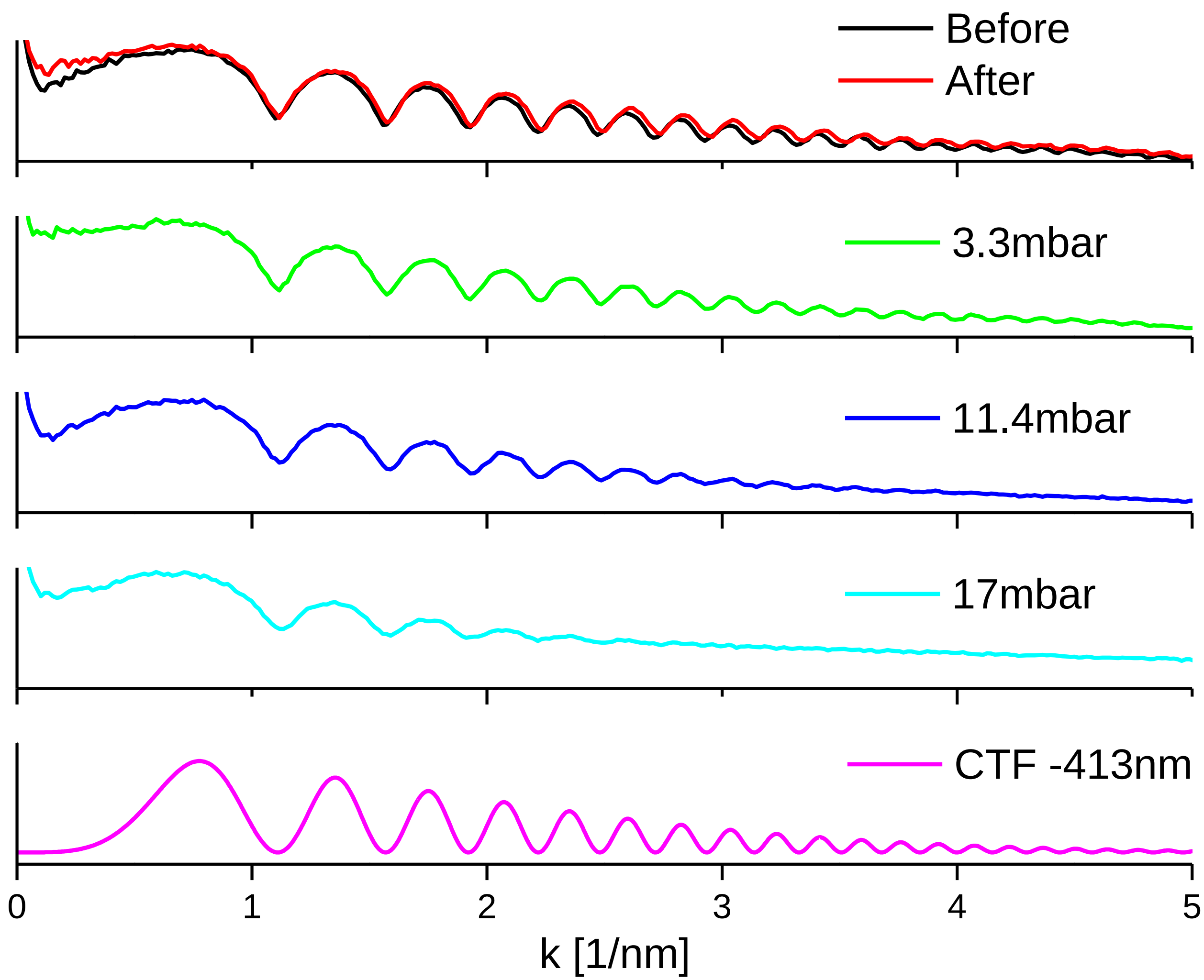






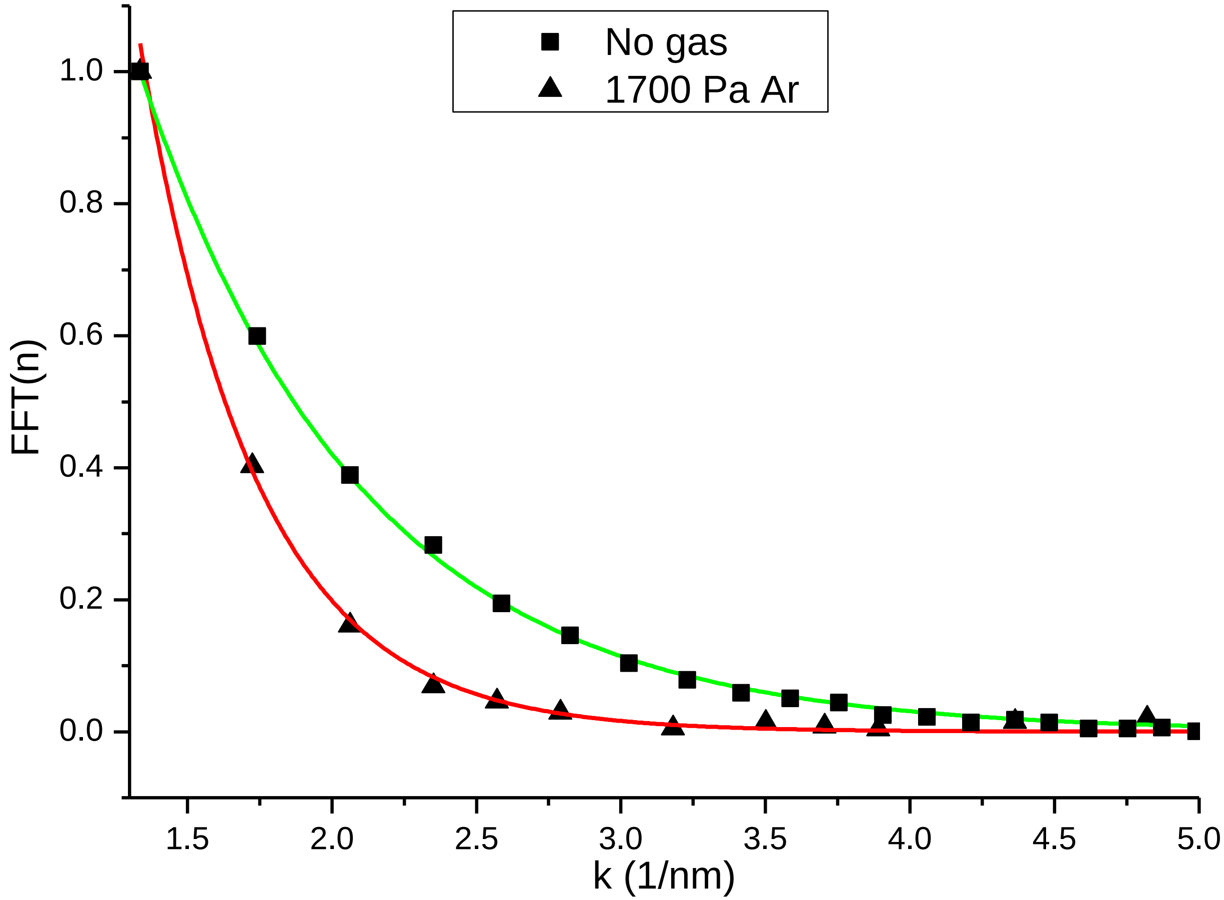
CTF in the Presence of Ar (300kV)

- In high vacuum (red), the power spectrum is almost identical to that calculated from ctfExplorer (purple)
- At low pressures, the effect is not observable (green)
- With increasing pressure, the damping becomes increasingly visible (blue and cyan)
- With lighter gas molecules, this effect is significantly lower
- An image was acquired in vacuum after the series (red) to ensure that the aC was not significantly damaged



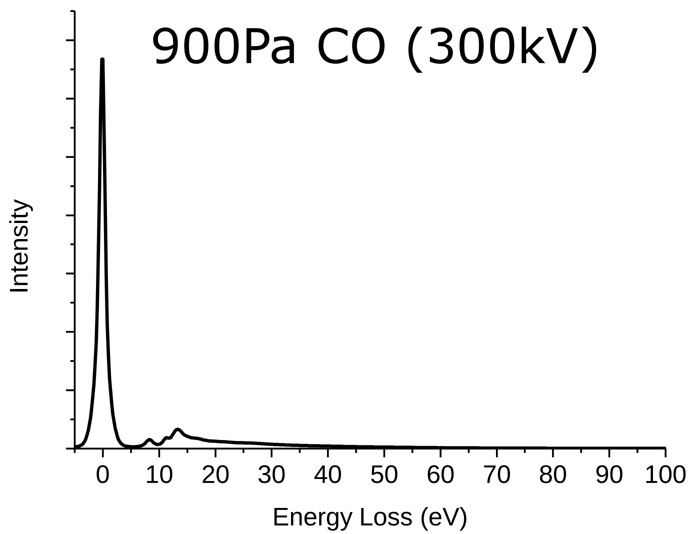
Fitting of Damping of FFTs in Ar (300kV)

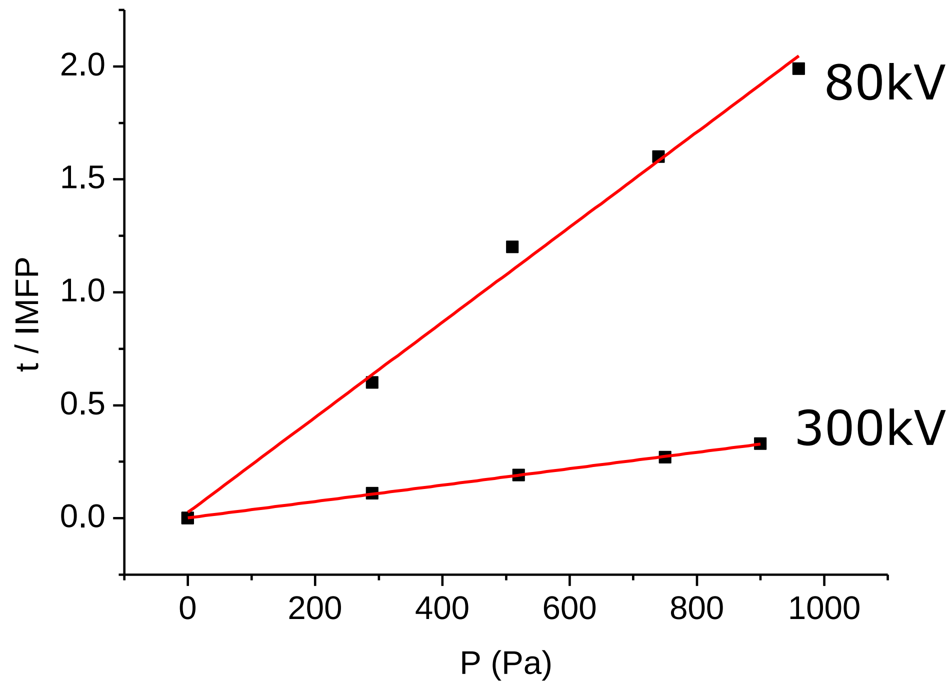
- The step height in the power spectrum is plotted as a function of k
- Each plot is fitted to an exponential decay
- At increased pressure, the step height decreases considerably faster



Gas composition and pressure by EELS

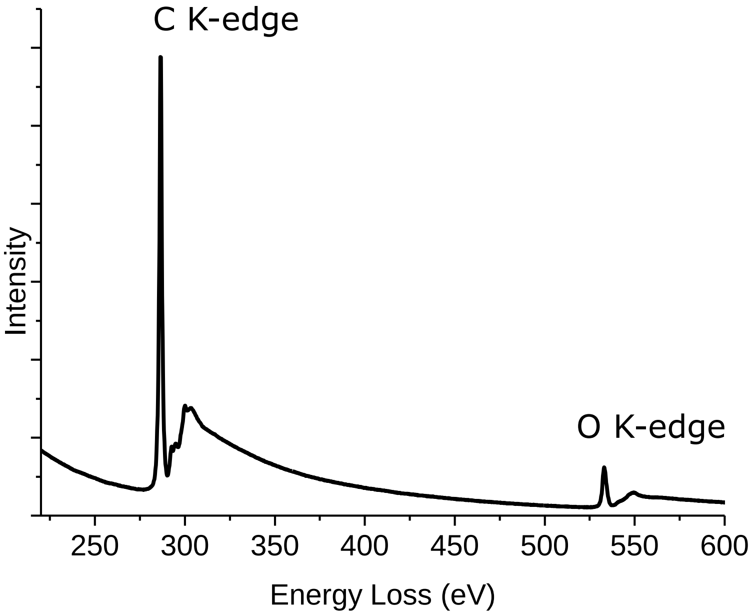
- Pressure (Low-loss EELS)
- Gas composition (Core-loss EELS)
- CO – EELS acquired in image mode
- IMFP is collection angle dependent

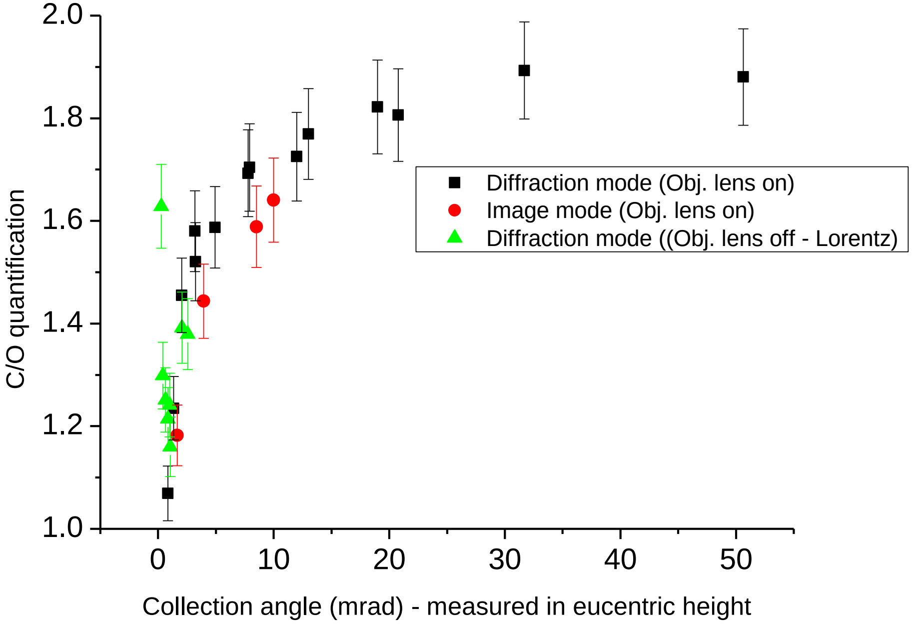




Gas composition and pressure by EELS

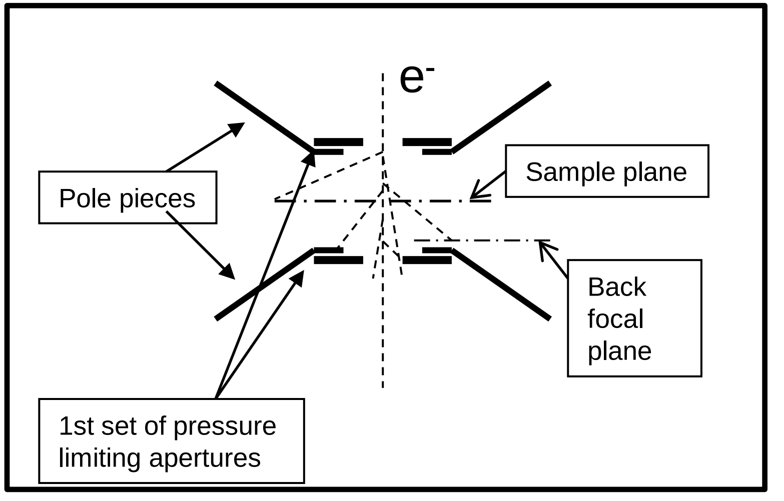
- CO – EELS acquired in image mode
- The collection angle is measured in the eucentric height





Apparent / mean collection angle (300kV)

- The measured collection angle makes little sense as the scattering occurs all over the pressurized volume



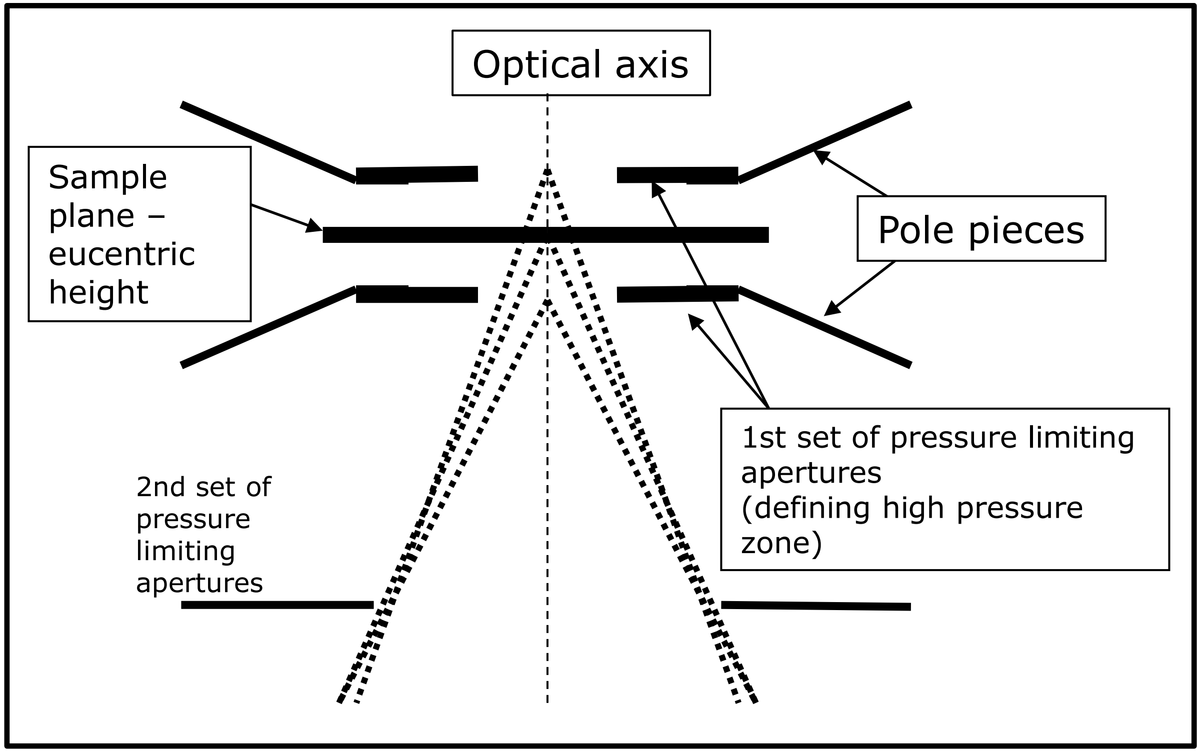
- The atomic ratio between carbon and oxygen calculated from the acquired spectra fits the theoretical value for small (~1 mrad) collection angles

- Consistent with the small ‘scattered contribution’ of gas to the image intensity – ‘high contrast of gas’

Angle resolved EELS

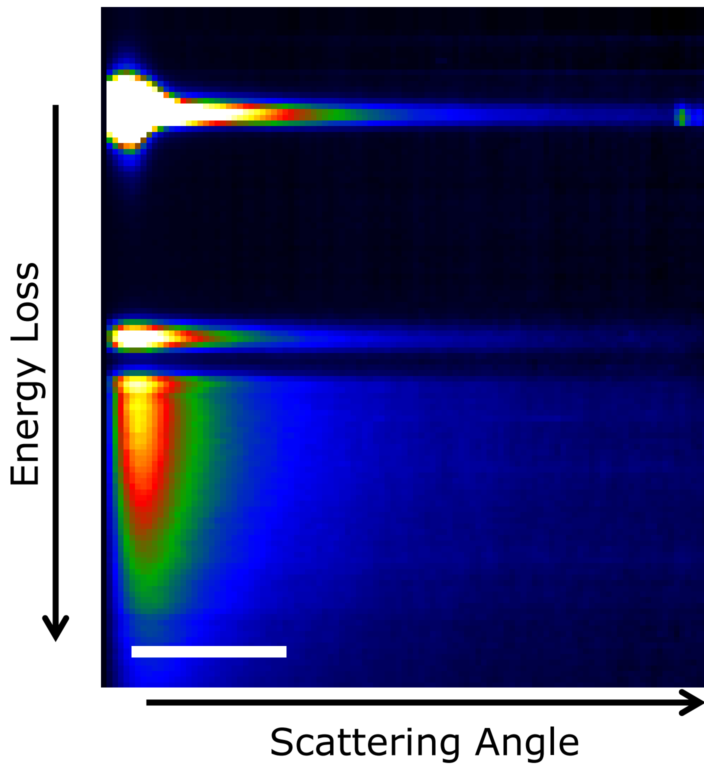
- Angle resolved EELS are acquired in Lorentz mode (objective lens off) to simplify scattering geometry

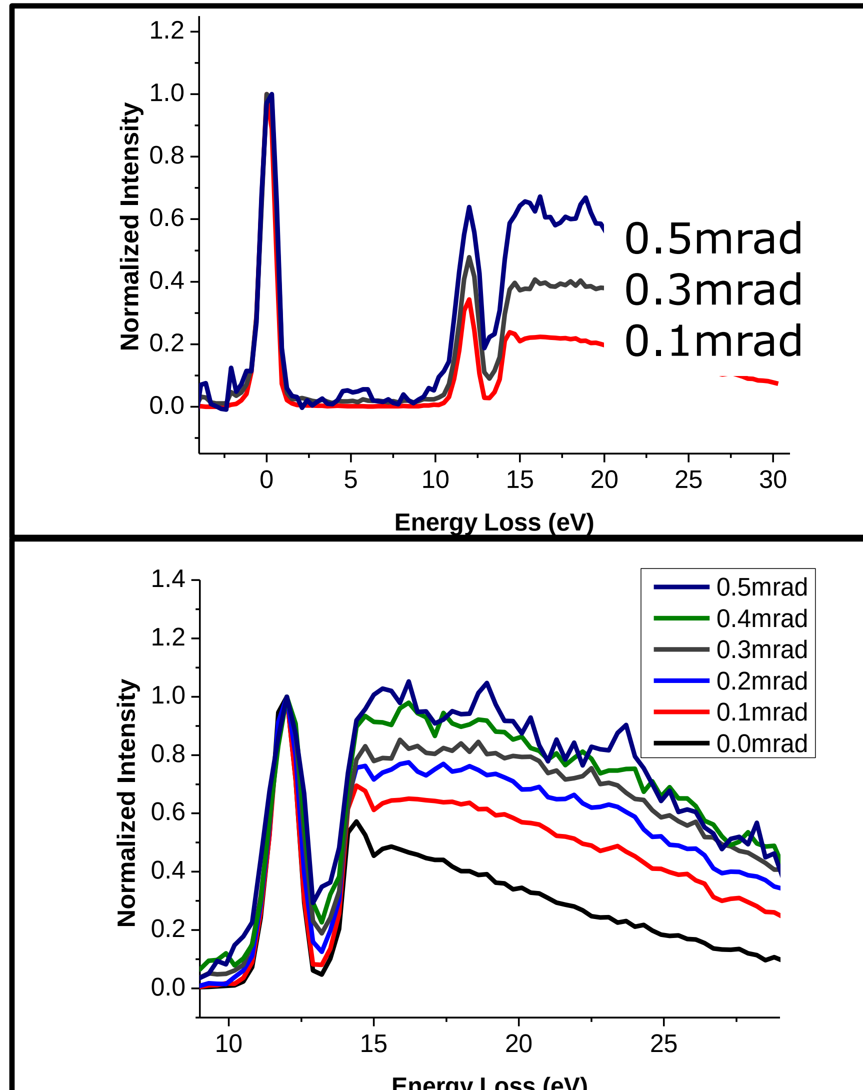
Broadening of scattering is usually less than 5%



Spectrum imaging (300kV) - Argon

- 1100Pa of Argon – no specimen
- Spectrum imaging with 0.3eV energy-selecting slit width
- Rotationally averaged



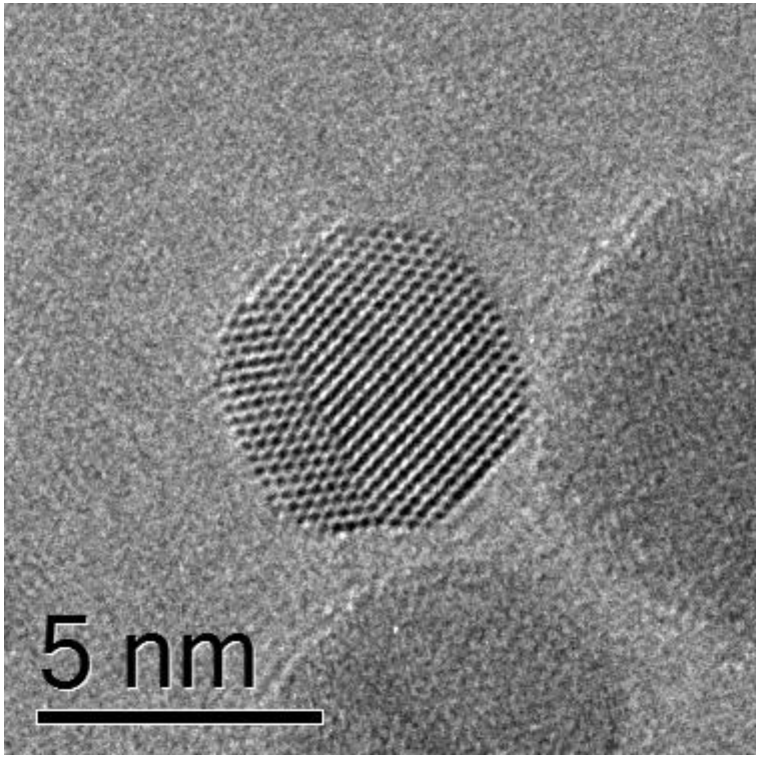


Beam Effects

- Electrons can ionize gas molecules making them more reactive
- Surfaces can be etched by reactive gas atoms, ions and molecules
  - S. Helveg *et al. J. Am. Chem. Soc.* **132**, 7968 (2010)
- Local heating in the electron beam
  - V. G. Gryaznov *et al. Phil. Mag. Lett.* **63**, 275 (1991)
- Knock-on damage altering atomic structure
- Sample ionization
- Sample charging and de-charging
  - Removal of charge from sample as in ESEM

Is abberration correction needed / useful in Environmental TEM?

- Yes, as interface regions (including surface regions) are not disturbed by delocalisation
- Au on graphene, P_{H_2} = 430Pa, RT
- Dynamics at interface / surface



Outlook and Challenges (Wish list)

- More to be done to understand the gas-electron interaction in the imaging process
- Detector efficiency
- Sample heating holders
  - Drift-free environment
  - Investigations while ON the heating ramp
  - Interference with electron beam
- Sealing technology
- Complementary *in situ* techniques
  - Light (Visible, IR, UV)
  - XRD (Transfer system)
- Sample heating and local temperature
  - The local temperature is a multi-parameter problem involving multiple sources and sinks